INSTRUCTIONS FOR COMPLET AFRL-SR-AR-TR-07-0022

REPORT DOCUMENTATION PAGE

1. REPORT DATE *(DD-MM-YYYY)* 09-01-2006	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* July 2005 to June 2006

4. TITLE AND SUBTITLE PICOSECOND COHERENT AND INCOHERENT DYNAMICS IN PROTEINS	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER FA9550-05-1-0431
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Robert H. Austin	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Trustees of Princeton University Office of Research and Project Admin 4 New South Building Princeton, NJ 08544-0036	**8. PERFORMING ORGANIZATION REPORT NUMBER** 0001
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) Air Force Office of Scientific Research 875 North Randolph St., Rm 3112 Arlington, VA 22203 Dr. howard schlossberg/NE	**10. SPONSOR/MONITOR'S ACRONYM(S)** AFOSR/PKA
	11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
DISTRIBUTION A. Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
There are two critical questions in the quantum protein dynamics: (1) the time scale of decoherence of coherent vibrational excitations of proteins and (2) the rate of transport of quantum vibrations along the amide I polymer chain. We have carried out a series of experiments at FELIX, a free-electron laser (FEL) in the Netherlands which attacked these critical questions. We found that there does not exist a highly narrow and long-lived coherent state in the amide I band, in spite of Austin's initial excitement that he had stumbled upon this effect. It remains a mystery why this large and narrow scattering signal appears exactly where one would NOT expect to see a temperature grating signal, namely at the temperature isosbestic point.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Robert H. Austin
U	U	U	U	17	**19b. TELEPONE NUMBER** (*Include area code*) 609-258-4353

Final Report: PICOSECOND COHERENT AND INCOHERENT DYNAMICS IN PROTEINS FA9550-05-1-0431

Robert H. Austin,
Department of Physics, Princeton University

Aihua Xie
Department of Physics, Oklahoma State University

1 Introduction

There are two critical questions in the quantum protein dynamics: (1) the time scale of decoherence of coherent vibrational excitations of proteins and (2) the rate of transport of quantum vibrations along the amide I polymer chain. We have carried out a series of experiments at FELIX, a free-electron laser (FEL) in the Netherlands which attacked these critical questions. One of the great advantages of the FELIX FEL is its ability to continuously vary the line width of the IR pulses by varying the cavity length. The grant we received from the AFOSR allowed us explore what happens when line width becomes very narrow (and hence the pulse width becomes very long). While it would seem to be a counterproductive thing to make very long pulses (10's of picoseconds, and hence linewidths of 0.1 cm^{-1}, there was a method to our madness.

We had discovered that in a pump-probe experiment in the amide-I band of a protein that narrowing the linewidth of the FEL resulted in a greatly enhanced pump-probe signal, but only in a narrow spectral region on the short-wavelength side of the amide-I peak. Fig. 1 shows the kind of pump-probe signal enhancement we observed with line narrowing of the FEL. At the

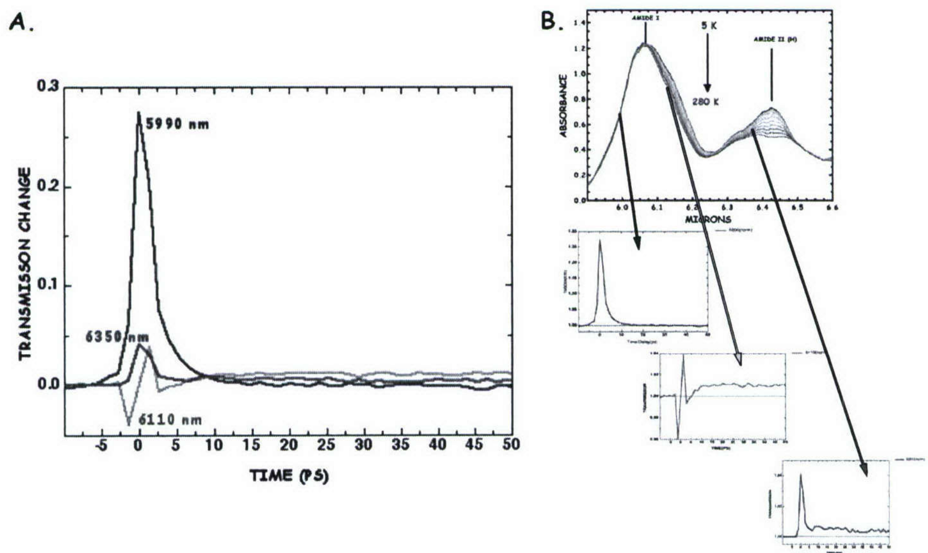

Figure 1: Pump-probe response of myoglobin as a function of wavelength in the amide I and II spectral regions. (A) Absolute transmission changes for 3 wavelengths vs. time. (B) Transmission changes plotted as a function of position of the amide I and amide II bands.

time we discovered this remarkable effect (Dec 2004) funding for this work from the MFEL program had ceased. We were left in the uncomfortable position of seeing a very large enhancement in apparent pump-probe signal, a severe disagreement with our colleagues at FELIX concerning the origin of this effect which was quite unexpected, and the lack of funding to at least do one more set of experiments to try and resolve the origin of the enhancement seen.

The controversy (well, it was a one side-sided controversy, Prof. Austin thought something remarkable was happening in terms of self-trapping of vibrational energy) came from the experimental fact that the anomalous pump-probe signal at the short wavelength side of the amide I band never showed any lifetime effects but instead looked like the autocorrelation of the pump beam with itself, as seen in Fig. 2. A self-trapped excitation should show an enhanced lifetime, while some sort of scattering artifact due to degenerate 4-wave mixing would be expected to appear as a autocorrelation signal. As the linewidth is narrowed in fact the pump-probe signal becomes more and more symmetric and appears to be an autocorrelation of the pump with itself.

2 Experiments

Two final experiments were done with the funds granted by the AFSOR in order to attempt to resolve this controversy

(1) A final run was done at FELIX in December 2005 to (1) measure the temperature dependence of simple oligoamino acids and test if simple oligoamino acids also had a similar large enhancement at certain spectral regions. If they do, then the impact of the Mb work would be several compromised.

(2) Photon echo experiments were done at Princeton University in June-August 2005 using a conventional OPA pumped by a regenerative amplified Ti:S system to test for long coherence times in the same spectral region as the enhanced pump-probe signal was seen.

I'll discuss the results of the Dec 2005 run first. We prepared a simple 3 amino acid oligonucleotide sample (tri-alanine). A full cryogenic temperature scan of the mid-IR absorbance spectrum revealed that like Mb and other proteins the absorbance spectrum is highly temperature dependent with a similar spectral region where there is no change in absorbance with temper-

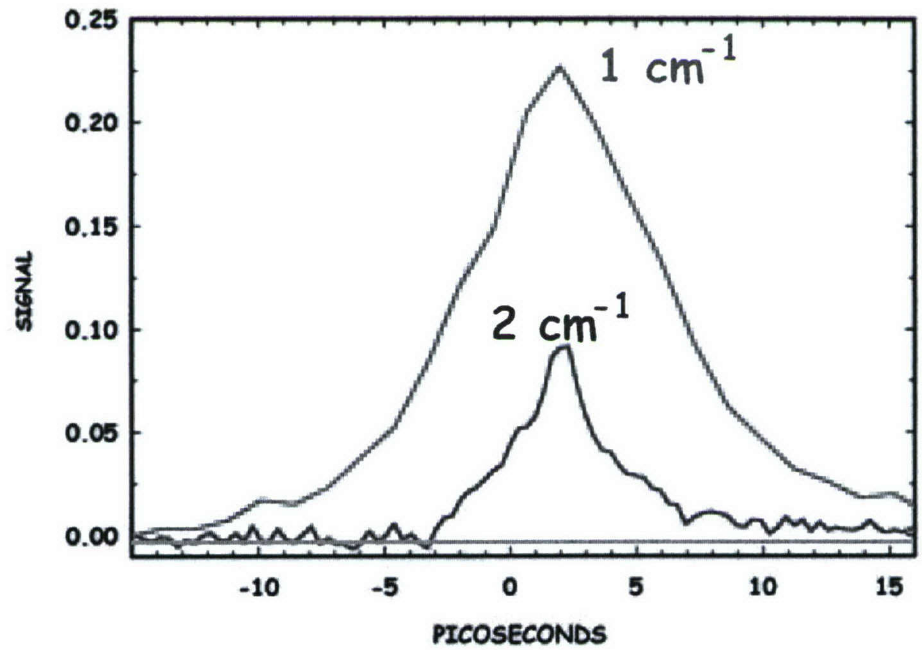

Figure 2: Pump-probe signal at 6.04 microns for a pulse of linewidth 2 cm^{-1} (blue) and 1 cm^{-1} (red). The green baseline shows the temperature dependence of the amide I that is picked up by the broader pulse.

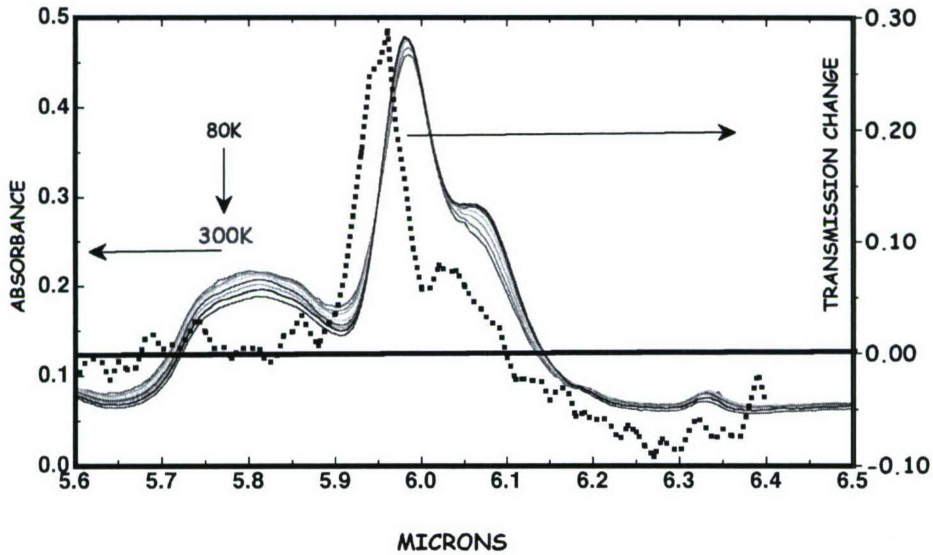

Figure 3: Results of the December 2005 FELIX run. The left hand axis and solid lines show the temperature dependence of tri-ala in deuterated glycerol, the right axis and the dashed lines show the pump-probe response of this sample.

ature over the 80K-300K range. We then did a pump-probe measurement at room temperature of the response of this simple sample and, as in the case of Mb, saw a large enhanced signal in a similar region of zero temperature dependence. See Fig. 3 for both the IR spectra and the pump-probe signals for the tri-alanine sample). Unfortunately, the large enhanced (30% transmission changes) and narrow width of the enhanced signal are very similar to the Mb signal (and also seen in other protein samples not shown here), indicating that this puzzling signal is not unique to highly folded proteins but rather occurs if there is a spectral region of no temperature dependence.

We also carried out a photon echo experiment at Princeton. This was a simple 2-beam photon echo experiment simply designed to check for any anomalous dephasing lifetime, at the start we were limited to the natural 5 cm^{-1} linewidth of the OPA and had made plans to use a subtractive dual monochromator. We did succeed in finding a photon echo signal in August

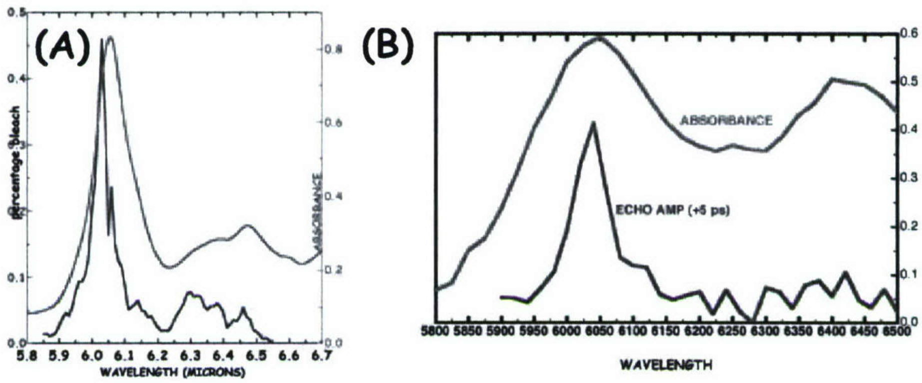

Figure 4: Results of the August 2005 Princeton run. (A) Observed pump-probe high resolution scan at FELIX of Mb. (B) Photon echo scan vs. wavelength of Mb done on the Princeton OPA configuration.

2005 at the expected place in a Mb sample, as shown in Fig. 4. However, time scan of the echo showed again basically an autocorrelation of the two pump signals with no long decoherence times, indicating that the signal was not due to a self-trapped state but rather was due to a transient coherent grating scatter.

3 Conclusions

It is disappointing that we were not able to show that there exist long-lived coherent states in the amide-I band of proteins. The FELIX work, which resulted in a series of nice papers, showed that long-lived states did exist in the amide 1 band [1], that vibrational energy could be transfered into the excited state vibrational manifold over a time period of 20 picoseconds [2] and that the far-IR spectral region showed unusually slow cooling times [3] that we still do not understand. However, it would appear from this work that there does not exist a highly narrow and long-lived coherent state in the amide I band, in spite of Austin's initial excitement that he had stumbled upon this. It remains a mystery why this large and narrow scattering signal appears exactly where one would NOT expect to see a temperature grating signal, namely at the temperature isosbestic point. We do not understand this mystery, and until at least Austin figures out this strange thing to his mind some questions remain very much open, certainly related to the far-infrared work

When Austin left FELIX at the end of the Dec. 2005 run it was with a heavy heart for he had not proven the origin of the scattering signal to his satisfaction and the issue of FIR dynamics was still open. The role of vibrational excitations and energy trapping in biology, IF THEY EXIST AT ALL, must we know think be in the FIR, not the amide I band. Probably the mid-IR modes lie far too high above kT at 300 K (300 cm-1) to be involved in thermally driven chemical reactions (this statement is probably wrong for photochemistry). We may have chased the wrong windmills, as the FELIX people made clear in the going-away present Austin got from his under the sea dwelling buddies (see Fig. 5), but....

We wish to thank the AFOSR for helping support this work, Dr. Britta Redlich and Dr. Lex van der Professor at FELIX for helping in the Dec 2005 FELIX run and Warren Warren of the Department of Chemistry at Princeton University and his excellent student Dan Fu for helping do the photon echo work.

The following paper was published using support from this grant:

Robert H. Austin, Aihua Xie, Lex van der Meer, Britta Redlich, Per-Anker Lindgrd, Hans Frauenfelder, and Dan Fu, Picosecond Thermometer in the Amide I Band of Myoglobin, Phys. Rev. Lett. 94, 12810-4 (2005)

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Thermometer in the Amide I Band of Myoglobin, Phys. Rev. Lett. 94, 12810-4

[3] A. Xie, A. van der Meer and R.H. Austin, (2002) Excited-State Lifetimes of Far-Infrared Collective Modes in Proteins, Phys. Rev. Lett. 88: 018102-1 - 018102-4

Figure 5: The farewell FELIX sweatshirt. The skinny Dutchman is Dr. Lex van der Meer.